Effect of Ultrasonic Pre-treatment on the Formation of DDR3 Zeolites

as Adsorbent of Carbon Dioxide Capture

By

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Dissertation submitted in partial fulfillment of

The requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering Department)

SEPTEMBER 2014

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CERTFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Yeong Yin Fong)

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SEPTEMBER 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Nur Syahirah Binti Mohamed Nazri

ABSTRACT

In the recent years, global concentration of carbon dioxide in the atmosphere has rapidly increased. The emission of carbon dioxide gives an impact on the global climate change. There are several commercially available process technologies which can be used for capturing CO_2 such as amine absorption, membrane separation and adsorption. Adsorption is the most preferable technology to be used as it shown great potential in CO_2 adsorption. Zeolites are amongst the most widely reported physical adsorbents for CO_2 capture in the research study and DDR3 zeolite is one of the promising material for CO2 adsorption. However, synthesis of DDR3 type zeolite is still a major concern due to it long synthesis duration which is up to 25 days. Therefore, this research work is focusing on the synthesis of DDR3 zeolite by using ultrasonic pre-treatment in order to reduce the crystallization time and increase the CO_2 adsorption capability while maintaining the morphology of the crystals. The resulting particles were characterized by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), and Fourier Transformed Infared (FTIR). The CO_2 adsorption characteristic of the resultant particles was analyzed by using CO_2 physisorption testing. The XRD results showed that the synthesis duration of the DDR3 zeolite has been successfully reduced to 1 day by introducing ultrasonic pretreatment method coupled with hydrothermal heating. Besides, the FESEM and FTIR results confirmed the morphology and structure of DDR3. However, based on the CO_2 physisorption testing, it showed that the adsorption capacity of DDR3 for all samples are more likely similar but are relatively low compared to the literature.

ACKNOWLEDGMENT

First and foremost, I would like to express my gratitude to God the Almighty for His blessing and mercy in completing my final year project.

I would like to express my sincere appreciation to my supervisor Dr. Yeong Yin Fong for her guidance and care throughout my project. She has been a very supportive supervisor during the entire project period. Her advices and guidance has always enlightened my idea in my research work. Beside that her professional comments and patience in reading my report countless time in order to make my thesis perfect are much appreciated.

Many big thanks to post graduate student, Muhammad Mubashir who is also under Dr Yeong's supervision for his unlimited guidance and support. He has been devoting so much in helping me to complete this dissertation.

I would also like to acknowledge to all the administrative staffs and technicians, who are willing to give me a hand throughout my research work without any reluctance. Also, their willingness to provide the facilities and entertain our demand during conducting the project.

My greatest thankfulness goes to my family who always being understanding and supportive during my undergraduate life. Last but not least, thanks to all the Universiti Teknologi PETRONAS involved lecturers and students who have been contributing great efforts and ides making this final year project a success.

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CHAPTER 1: INTRODUCTION

1.1 Background of Study

The major greenhouse gas which is carbon dioxide becomes the biggest contributor to global warming. The carbon dioxide emitted to atmosphere has been classified as a major contributor to this problem. Carbon dioxide sources are divided into two categories which are natural source and human source. As comparison, natural sources of carbon dioxide are more than 20 times larger than sources due to human activity. Consequently, the natural sources are closely balanced by natural sinks. Human source includes the combustion of fossil fuels such as coal, natural gas, petroleum. In addition, carbon dioxide also used in industrial processes such as power plants, oil refining and the production of cement, iron and steel. Also, in petrochemical industries, the carbon dioxide has been used for production of limited chemicals such as urea. These lead to the increasing of CO_2 concentration in atmosphere from 280ppm in 1800 to 390 ppm in 2010 (Songolzadeh, Ravanchi, & Soleimani, 2012).

Meanwhile, Energy Information Administration (EIA) 2010 predicted a 49% increase of energy demand from 2007 to 2035 following more and more countries becoming industrialized ("International Energy Outlook," 2010). The International Energy Outlook 2010 (IEO2010) reference case reported that the world energy-related carbon dioxide (CO_2) emissions increased from 29.7 billion metric tons in 2007 to 33.8 billion metric tons in 2020 and 42.4 billion metric tons in 2035 ("International Energy Outlook," 2010).

The greenhouse gases (GHG) effect is one of the most challenging environmental issues lead to the implications of GHG for global climate change. Among these GHG, CO_2 is the largest contributor in regard of its amount present in the atmosphere contributing to 60% of global warming effects, although methane and

chlorofluorocarbons have much higher greenhouse effect as per mass of gases (Yamasaki, 2003).

In order to reduce the emission, the carbon dioxide capture technologies play the important role. Various technologies such as absorption, adsorption, and membrane separation have been reported for CO_2 capture (Songolzadeh et al., 2012). As reported by IPCC (2005), membranes processes are used for CO_2 capture from natural gas at high pressure and at high CO_2 concentration. The removal of carbon dioxide using commercially available polymeric gas separation membranes results in higher energy penalties on the power generation efficiency compared to standard chemical absorption process (Herzog, Golomb, & Zemba, 1991). Meanwhile, for the absorption or stripping process, amine solutions such as MEA is been used, which is a commercialized technology in natural gas industry for 60 years and is regarded as the most mature process. Besides MEA, diethanolamine (DEA) and methyldiethanolamine (MDEA) are often used as absorbents (Yang, Xu, Fan, & Gupta, 2008).

Clean Air Technology Centre (CATC) reported the adsorbed material is held physically, rather loosely, and can be released rather easily by either heat or vacuum. In contrast, an absorber reacts chemically with the substance being absorbed, and subsequently the absorbed substance can be hold much more strongly which require more energy to release the absorbed substance.

Porous materials synthesis has recently focused on the creation of functional materials tailored to specific processes through directed assembly strategies. Zeolite and mesoporous are the best examples to implement the effort. Those involved the phase change from the gel or solution phase in the controlled condensation of silica. Also, it has been stated that the zeolites with pores below 1 nm show best performance in separations and catalysis (Fedeyko, Vlachos, & Lobo, 2006).

The widely used adsorption processes includes the metal oxide, molecular sieves and promoted hydrotalcites based processes. The molecular sieves which included zeolite

and activated carbon are the examples of adsorbents used. Zeolite systems can produce nearly pure streams of CO_2, but the method is costly due to vacuum pumps and dehumidification equipment (Shimekit & Mukhtar, 2012). As most effective adsorbent, the use of hydrotalcites at high temperatures (177-327°C) is widely for adsorption of CO_2 in or near combustion or gasification chambers.

Tremendously interests have been focused on the study of zeolite as adsorbent. Pure silica zeolites have important practical advantages over the traditional cationic zeolites since they are hydrophobic and have low catalytic activity (Vidoni, 2004). However, Clean Air Technology Centre (CATC) stated that the hydrophobic zeolite which can also be synthesized in crystals from 1 micron to 1 millimeter in diameter, and these can be bonded into larger granules to lower the resistance to air flow. Since synthesis is expensive, it is usually reserved for making either hydrophobic zeolite or zeolite catalysts with a specific large pore size.

DDR or DDR3, which is short-form for Decadodecasils 3R, was first developed in 80's by (Gies, 1986) who developed the synthesis and established the crystal structure of this material. The pore system comprises relatively large (19-hedral) cages interconnected through 8-ring windows with aperture approximately 3.6 x 4.4 Å. This window size makes DDR3 an attractive candidate for CO_2/CH_4 separations as the critical window diameter (0.36 Å) falls between the critical diameters of methane (0.38 Å) and carbon dioxide (0.33 Å), as required for size selective molecular sieve separation (Vidoni, 2004).

In the present work, DDR3 zeolite crystals were synthesized via hydrothermal heating method coupled with ultrasonic pre-treatment. The durations of hydrothermal heating were varied from 0.5-10 days and the temperature was maintained at 160^{o}C. Meanwhile, the durations of ultrasonic pre-treatment were varied from 1-3 h.

1.2 Problem Statement

The synthesis of DDR3 zeolite required a long duration, typically 25 days (Bose, Sen, Das, & Das, 2014). It has been found that the application of ultrasonic pretreatment will lead to the reduction of crystallization time of DDR3 zeolite membrane at room temperature (Bose et al., 2014). Subsequently, the DDR3 membranes were synthesized on the seeded support within 5 days by sonication mediated hydrothermal technique. However, there are still no reports on the preparation of DDR3 zeolite crystal based on the same technique. Therefore, this project is focused on how ultrasonic pretreatment can affect the formation of DDR3 particles. The technique will be further explained in methodology part.

1.3 Objectives and Scope of Study

The objectives and scopes of this project are:

1. To synthesis DDR3 zeolite crystals using ultrasonic pretreatment method
2. To characterize DDR3 zeolite by using X-Ray Diffraction (XRD), Fourier Transformed Infared (FTIR) and Field Emission Scanning Electron Microscope (FESEM)
3. To test the performance of DDR3 zeolite as an adsorbent for carbon dioxide using CO_2 physisorption (BELSORP)

1.4 Relevancy and Feasibility of Project

The relevancy of this project is to obtain a feasible method and optimum ultrasonic pre-treatment parameters for synthesis DDR3 zeolite. By obtaining optimum synthesis parameters, the crystallization time of DDR3 zeolite is expected to be reduced.

By proper planning and execution, this project can be completed as per scope before the date submission as the synthesis of crystal take only less time.

CHAPTER 2: LITERATURE REVIEW

2.1 Importance of carbon dioxide removal

The 20th century has seen the rapid increase of population and extremely growth in consumption of energy. The increasing industrialized companies lead to higher energy that be consumed in 21st century. Air toxics and greenhouse gases (GHG) which gives major contribution to global problems are now become environmental issues because of the pollutant emitted from combustion of fossil fuels. Yamasaki (2003) stated that the research that has been made for the past five decades which causes global warming mainly due to the rising of GHG levels in atmosphere. CO_2 which included as GHG source become the largest contributor of about 60 percent of the effect due to global warming (Yamasaki, 2003).

While renewable energy will reduce the CO_2 emission in the long term, by switching the energy resource from the current fossil fuel based toward to emerging solar, biomass, wind and tides, CO_2 capture and sequestration from the large stationary coal or natural fired power plants, cement plants, oil refineries and steel plants, will reduce CO_2 emission in the intermediate time span. Therefore, CO_2 capture from the post combustion facilities, which does not need significant modification of the current industrial infrastructures, has aroused more research interests and industrial attentions (Shuangzhen & Xiaochun, 2012).

On top of that, International Panel on Climate Change (IPCC) predicts that, by the year 2100, the atmosphere may contain up to 570 ppmv CO_2, which will lead to increasing of mean global temperature of around 1.9°C and also increase in mean sea level of 38 m (Stewart & Hessami, 2005). IPCC also reported in natural gas, the presence of CO_2 contaminants in gas stream is about 70% high. Unfortunately, the specifications of pipeline given for natural gas only require a CO_2 concentration below 2-3%. Hence, this CO_2 must be removed from natural gas because it can reduce the heating value and energy content of the gas (International Panel on Climate Change, 2005)

The CO_2 capture may be an option to reduce the CO_2 emission from today's industries. Many researchers have targeted at improving the current technologies or developing new approaches of CO_2 separation and capture (Yang et al., 2008).

2.2 Existing technology in CO_2 removal

There are many dedicated researches trying to improve the current technologies and develop new methods for CO_2 capture. There are several different techniques which can be used for CO_2 capture, such as chemical and physical absorption, adsorption, and membrane separation, but the choice of a suitable method is mainly depending on the characteristics of the gas to be treated as well as the process conditions.

Adsorption is a physical process that involves the attachment of a gas or liquid to a solid surface. Adsorption can reduce energy and cost of the capture or separation of CO_2 in post-combustion capture. However, the success of this approach is dependent on the development of an easily regenerated and durable adsorbent with high CO_2 selectivity and adsorption capacities (Songolzadeh et al., 2012).

For membranes, they are already an alternative and competitive technology for selected gas separation processes (He & Hagg, 2011). Gas separation membranes allow one component in a gas stream to pass through faster than the others. There are many different types of gas separation membrane, including porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. Recent research directed at the development and application of inorganic membranes is advancing faster because of the demand in new application fields, such as fuel cells, membrane reactors, and other high-temperature separations. Inorganic or polymeric membrane separation processes are expected to be more efficient that conventional CO_2 separation processes (Damle & Dorchak, 2001).

Tomita et al. (2007) reported that a widely used technology for CO_2 removal is amine adsorption. However, amine plants are complex and costly. Membrane separation is energy-efficient which the reason why many membranes have been

developed for CO_2 separation. The easy operation, reliable performance and easy scale up have made polymer membrane as favorite media to capture CO_2 from post combustion. Historically, polymer membrane has been applied successfully in ammonia synthesis/purge, petrochemical/refinery and CO_2 separation on industrial scale in the recent 30 years (Shuangzhen & Xiaochun, 2012). Furthermore, polymeric membranes might be less stable for CO_2/CH_4 separation at high temperatures and high CO_2 pressures. Inorganic membranes, especially zeolite membranes, offer the potential of a breakthrough development that anticipate those disadvantages.

2.3 Zeolites and DDR3 Type zeolite

Zeolites are the most commonly used adsorbents. They are used for wastewater treatment, gas cleaning and many more gas/liquid separations. Zeolites take out the impurities, by surface interactions between the zeolite and the impurities, and also by molecular sieving. Zeolites are hydrated alumininosilicate of metals like sodium, potassium and magnesium.

Zeolites are crystalline, hydrated aluminosilicate compounds with well-defined pores having superior thermal, mechanical, chemical and high pressure stability. They have three dimensional structures built by AlO_4 and SiO_2 tetrahedral. Oxygen atoms link the adjacent tetrahedral. Well defined channels and cavities as well as morphology and crystal size of these compounds have an important role for their specific applications in industries (Hassani, Salehirad, Aghabozorg, & Sobat, 2010).

Zeolite membranes are a special class of porous inorganic membranes with well-defined intracrystalline pores. They have superior thermal, mechanical, chemical and high pressure stability. Small pore zeolite membranes have the potential to separate light gases based on molecular sieving effects. Decadodecasil 3R (DDR) framework, having pore diameter 0.36 x 0.43 nm, an efficient member of zeolite family, has been studied for various applications and most notably has shown excellent performance

in H_2 gas separations from other light gases like CO_2, N_2, CH_4 and others (Bose et al., 2014).

In recent years, considerable effort has been directed into synthesis of zeolite membranes (Zheng, Hall, & Guliants, 2008). Numerous eight-membered-ring zeolites with small pores have been examined as candidates for adsorbents that are useful or the separation of small molecules. Small-pore zeolites, such as zeolite T, SAPO-34, and DDR3, have pores that have the size that is similar to that of the CH_4 molecule, but which are larger than the CO_2 molecule. For that reason, they are suitable for CO_2/CH_4 separation. High-silica types offer the advantage of hydrophobicity which they retain their adsorption capacity in water (Tomita, Suzuki, Nakayama, Yajima, & Yoshida, 2007). Figure 1 shows the building block and framework of DDR3 zeolite crystals.

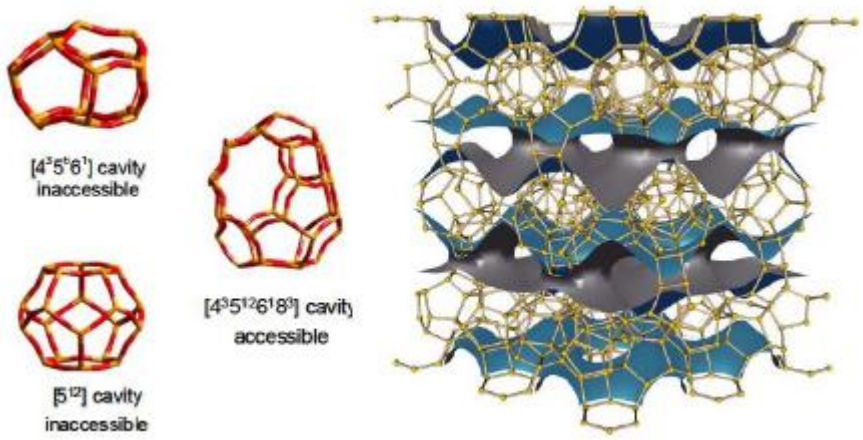

Figure 1: Building blocks and framework of DDR3 zeolite crystals

2.4 Comparison between other adsorbents and DDR3 zeolites

According to Alessandro et al. (2010) solid physical adsorbents which are in packed or fluidized adsorbent beds, possess significant advantages for energy efficiency compared with chemical and physical absorption approaches. In the case of adsorbents, however, there may be some practical difficulties in achieving the same heat exchange efficiency in the cycle between the hot and cold sections of the capture process.

A key concern for physical adsorbents is balancing a strong affinity for removing an undesired component from a gas mixture with the energy consumption required for their regeneration. A variety of solid physical adsorbents have been considered for CO_2 capture including microporous and mesoporous materials, metal oxides, and hydrotalcite like compounds, amongst others (D'Alessandro, Smith, & Long, 2010).

As stated by Songolzadeh et al. (2012) coal is one of the adsorbent used for CO_2 capture. The ability for coal to adsorb CO_2 depends on its affinity, ash, and porosity. All technologies introduced have their advantages and disadvantages depending on the aim of the process. Hence, other than establishing new technologies, the exploration of capture materials with high separation performance and low capital cost are also need to take into consideration(Songolzadeh et al., 2012). Generally, the quality of CO_2 adsorbent must have high selectivity and adsorption capacity, kinetics, adequate adsorption, remain stable after adsorption and obtain good thermal and mechanical stability as well.

Anthracites are known to produce high surface area activated carbon. Maroto-Valer et al. (2005) studied the CO_2 capture behavior. They found that CO_2 capture does not show a linear relationship with the surface area. The highest CO_2 adsorption capacity was 65.7 mg CO_2/g adsorbent for the anthracite activated at 800°C for 2 h with a surface area of 540 m^2/g. The anthracite with the highest surface area of 1,071 m^2/g only had a CO_2 adsorption capacity of 40 mg CO_2/g adsorbent. This could be explained by certain size pores being effective for CO_2 adsorption (Maroto-Valer,

Tang, & Zhang, 2005). Also, tables below show the performance of other adsorbents on CO_2 capture. Table 1 shows CO_2 adsorption capacities of different zeolites.

Table 1: CO_2 adsorption capacities of different zeolites

Zeolite type(Choi, Drese, & Jones, 2009)	T(K)	Pco_2	q(mmol.g^{-1})
DDR zeolite	296	1.2	1.2
SAPO-34	295	1	2.50
13 X	393	0.15	0.7
5A	393	0.15	0.38
4A	393	0.15	0.5
WEG-592	393	0.15	0.6
APG-II	393	0.15	0.38
Na-Y	273	0.1	4.9
Na-X	373	1	1.24
NaX-h	323	1	2.52
NaX-h	373	1	1.37
Na-X-c	323	1	2.14
Na-X-c	373	1	1.41
Cs-X-h	323	1	2.42
Cs-X-h	373	1	1.48
Cs-X-c	323	1	1.76
Cs-X-c	373	1	1.15

2.5 Synthesis of DDR particles

In 1986, Gies reported the synthesis of DDR3 zeolite particles for the first time (Gies, 1986). In 1994, Exter et al. (1996) optimized the synthesis duration, water concentration and conventional heating temperature for obtaining DDR3 zeolite crystals. They successfully synthesized DDR3 crystals in 25 days at 160 °C using tetramethoxysilane (TMOS) as a silica source (Exter, Jansen, Bekkum, & Zikanova, 1997). Subsequently, Tomita et al. (2004) reported the synthesis of DDR3 zeolite particles following the method reported by Exter (Tomita, Nakayama, & Sakai, 2004). Qi-Liang et al. (2009) synthesized DDR3 crystals in 9 days using fluoride medium in order to study the effect of synthesis conditions on the crystals size (Qi-Liang, Sheng-Lai, & L. Xiao, 2009).

Bose et al. (2014) has successfully synthesized DDR3 crystals in 5 days at room temperature by sonication mediated hydrothermal technique on the synthesis solution for 3h and Ludox-40 as silica source prior to the crystallization of DDR3 particles (Bose et al., 2014). The sonication mediated method applied the ultrasound to chemical reactions thus will lead to homogenous nucleation and will reduce the crystallization time at room temperature compared to conventional chemical methods. This method also possess high energy acoustic cavitations are formed when liquids are subjected to ultrasonic pre-treatment (Bose et al., 2014).

Various researchers had successfully reduced the synthesis duration of zeolites for example MCM-22, zeolite ANA, B-ZSM-5, SaPO-34, NaP, and zeolite-T using ultrasonic pre-treatment. Wu et al. (2008) reported the ultrasonic assisted aging effect on zeolite MCM-22 gel. It was observed that without aging any process, crystallization time of MCM-22 was 120 h, while using ultrasound pre-treatment treatment, MCM-22 can be synthesized in 48 h (Wu, Ren, & Wang, 2008). Subsequently, Azizi et al. (2010) studied the effect of static and ultrasonic aging on synthesis of analcime (ANA) zeolite. They reported that crystallization time of ANA zeolite can be reduced from 96 h to 48 h, using ultrasonic pre-treatment. It was also concluded that the increase in ultrasonic aging time can leads to transformation of

spherical ANA zeolite into rod-like ANA zeolite (Azizi & Yousefpour, 2010). Meanwhile, Abrishamkaret et al. (2010) found that ultrasound assisted aging, could significantly reduce crystallization time of B-ZSM-5. They reported B-ZSM-5 zeolite can be synthesized in 18 h using ultrasonic pre-treatment (Abrishamkar, Azizi, & Kazemian, 2010).

Askari et al. (2011) successfully synthesized SAPO-34 zeolite in 1.5 h using ultrasonic pre-treatment. The average crystal size of the final product prepared using ultrasonic pre-treatment was 50 nm that is much smaller than that of synthesized under hydrothermal condition and the morphology of the crystals changed from uniform spherical nanoparticles to spherical cube SAPO-34 crystals respectively (Askari & Halladj, 2011). Subsequently, Pal et al. (2013) reported the synthesis of NaP zeolite crystals at room temperature and shorten crystallization time using ultrasonic pre-treatment method. They successfully reduced the synthesis duration of NaP zeolite from 24 h to 3 h. The effect of ultrasonic energy and pre-treatment time showed that with increasing sonication energy, the crystallinity of the powders decreased but phase purity remain unchanged (Pal, Das, Das, & Bandyopadhyay, 2013). Recently, Yeong et al. (2014) investigated ultrasonic pre-treatment effect on synthesis duration of zeolite T. They successfully reduced synthesis duration from 7 days (168 h) to 3 days (72 h) by introducing ultrasonic pre-treatment method (Yeong, Novichaka, Lai, Lau, & Azmi, 2014). From all above successful cases, it is concluded that ultra-sonic pre-treatment can significantly reduce the synthesis duration of zeolites. Table 3 shows the effect of ultrasonic pre-treatment on zeolites reported by various researchers.

DDR3 crystals required very long synthesis duration, as it consumed 25 days using conventional hydrothermal growth method. Researchers are yet to put their focus on DDR3 crystals because of synthesis time constraints. The ways to reduce the synthesis duration of DDR3 crystals still remain a challenging issue. Therefore, a facile method to reduce the synthesis duration of DDR3 crystal prior to membrane

formation is very crucial in order to reduce the overall synthesis duration of DDR3 membrane.

Sonochemistry is based on acoustic cavitation that is the formation, growth and collapse of bubbles in a liquid. In addition to above methods, sonochemical synthesis by ultrasonic pre-treatment (20 kHz–10 MHz is a new method for synthesis of nanoparticles especially nanocatalysis. Also method can be used for industrial scale and recently there are some activities in this field. In this method, the size of particles can be easily controlled by changing the ultrasound-related variables. Chemical effects of ultrasonic waves are due to acoustic cavitation phenomena in the solution. This method, high energy acoustic cavitations are formed when liquids are subjected to ultrasonic pre-treatment (Askari & Halladj, 2011). Cavitation is the formation, growth and implosive collapse of bubbles in liquid (Bose et al., 2014). Due to collapse of bubbles, a temperature and pressure of about 5000–25,000 K and 181.8 MPa are produced. Such a high temperature breaks the chemical bonds and consequently, causes the reactions to proceed (Askari & Halladj, 2011).

Askari et al. (2011) reported that, because of cavitation effect which will cause high temperature and high pressure in a solution, the ultrasonic treatment can influence the crystallization kinetics and the formation of crystal nuclei. Ultrasound seems to also influence the physicochemical phenomena related to nucleation and crystal growth, occurring during crystallization. Applying ultrasound was also shown to affect the primary nucleation of potassium sulphate, by leading to reductions in the induction time and the metastable zone width of this material (Askari & Halladj, 2011).

Previously, same method applied to synthesis silicoaluminophosphate molecular sieves SAPO-34 nanocrystal. This SAPO have considerable potential as acidic catalyst which can act as adsorbent in reactions and catalyst in petrochemical reactions (Julian, Michael, & Rajiv, 1997). It has been reported that the effectiveness of the SAPO-34 catalysts are improved by reducing their crystallite size (Nishiyama et al., 2009). In sonochemical process, ultrasonic waves will be formed from

collapsing of bubbles. This collapsing of bubbles occurred in decreasing temperature with a high rate. Consequently, it prevents agglomeration of particles and smaller size crystal will be produced (Askari & Halladj, 2011). This method of using ultrasound was successful in synthesizing SAPO-34 which produced high crystallinity with a large specific area (Askari & Halladj, 2011). SAPO-34 shows the highest adsorption capacities m however, the moisture stability is low. It cannot stand the moisture (Tomita et al., 2007). Compared to DDR3, which is pure silica and it can stand the moisture due to its hydrophobic properties which allow it to retain its adsorption capacity when water present. That is the reason, DDR3 zeolite is chosen as adsorbents.

On top of that, this method which is used on DDR3 membrane and other zeolites can be applied on DDR3 crystals as well. It can be seen that ultrasound can enhance the chemical reactions, nucleation and growth of precipitates (Feng & Li, 1992). Therefore, this project is mainly focus on how this ultrasonic pre-treatment can apply in synthesis of DDR3 crystals and also how efficient it would be as adsorbents for carbon dioxide.

Table 2: Effect of ultrasonic pre-treatment on zeolites reported by various researchers

Material	Synthesis Duration (h) with sonication	Synthesis Duration (h) without sonication	References
MCM-22	48	120	(Wu et al., 2008)
Zeolite ANA	48	96	(Azizi & Yousefpour, 2010)
B-ZSM-5	18	120	(Abrishamkar et al., 2010)
SAPO-34	1.5	24	(Askari & Halladj, 2011)
NaP	3	24	(Pal et al., 2013)
Zeolite – T	72	168	(Yeong et al., 2014)

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

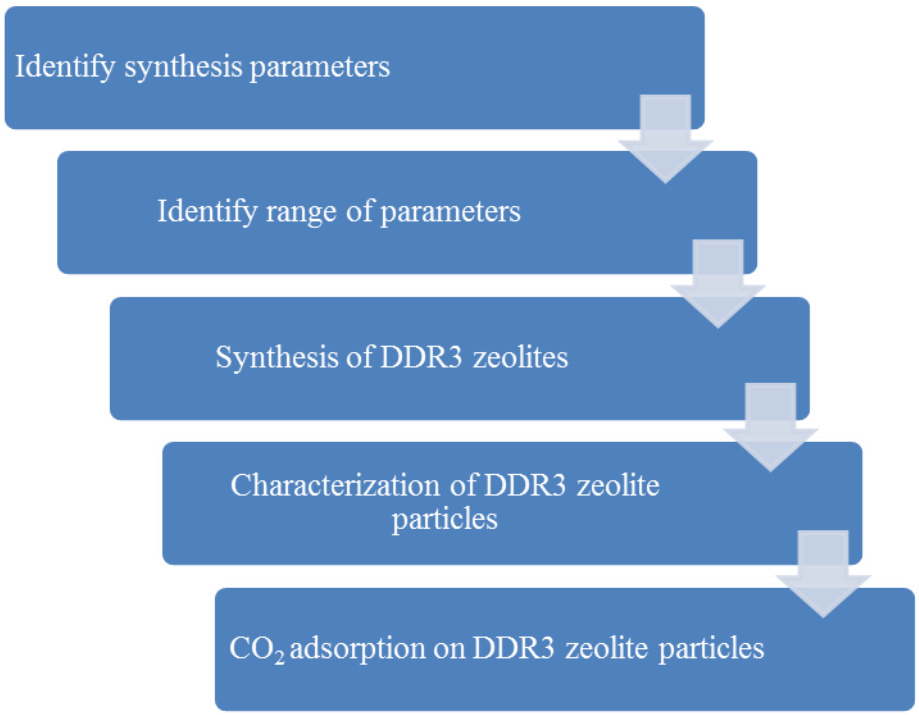

Figure 2: The research methodology for this project

Figure 2 shows the overall research methodology of the present work. Based on Figure 2, there are several steps of activities that need to be performed in order to achieve the objectives. The first step is to identify the synthesis parameters of DDR particles and the second stage is to identify range of parameters. Next stage is to synthesis the DDR zeolites by applying the ultrasonic pretreatment method. After that, the DDR zeolite particles will be characterized by using XRD, FESEM and FTIR. Lastly, the CO_2 adsorption on DDR zeolite particles will be tested in order to study the effect of the CO_2 adsorption capability by using CO_2 physisorption (BELSORP). Details on each stage will further be discussed in the next section.

3.2 Experimental

The experimental procedures in synthesis of DDR3 zeolite are as follows:

3.2.1 Synthesis of DDR3 zeolite seeds

1. The molar composition of the sol used for the synthesis was:
   100 silica (tetramethoxysilane,TMOS) : 47 1-adamantanamine : 404 ethylene diamine: 11240 deionized water
2. 1-adamantanaminewas prepared with adding ethylene diamine and deionized water
3. The mixture was stirred for 1 hour.
4. The mixture was heated at 95℃ for 1 hour with continuous stirring (Figure 3).

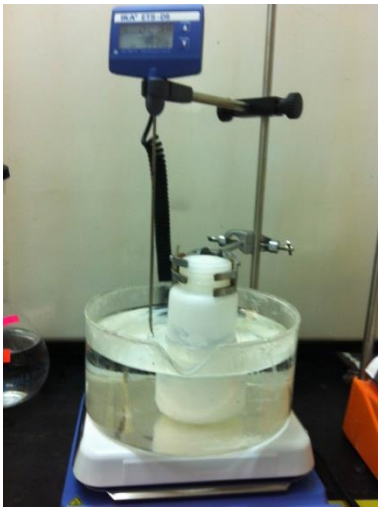

Figure 3: Mixture is heated with continuous stirring

5. The mixture was then cooled down with ice for 20 minutes.
6. TMOS was then added to the mixture drop by drop.
7. The mixture was heated again to 95℃ for 3 hours until the solution become clear.
8. The resulting mixture is then sonicated for required hours (Figure 4).

Figure 4: Sonication process of mixture

9. The synthesis solution was transferred to Teflon-lined reactor vessel for hydrothermal growth at 160 ℃

Figure 5: Solution in Teflon-lined reactor vessel which is placed in oven for hydrothermal growth

10. Table 3 shows the samples which were synthesized in the present work.

Table 3: Synthesis parameters in the present work

Sample	Ultrasonic pretreatment duration, h	Hydrothermal growth duration, days
Sample 1	-	25
Sample 2	3	10
Sample 3	2	5
Sample 4	1	5
Sample 5	1	2
Sample 6	1	1
Sample 7	1	0.5

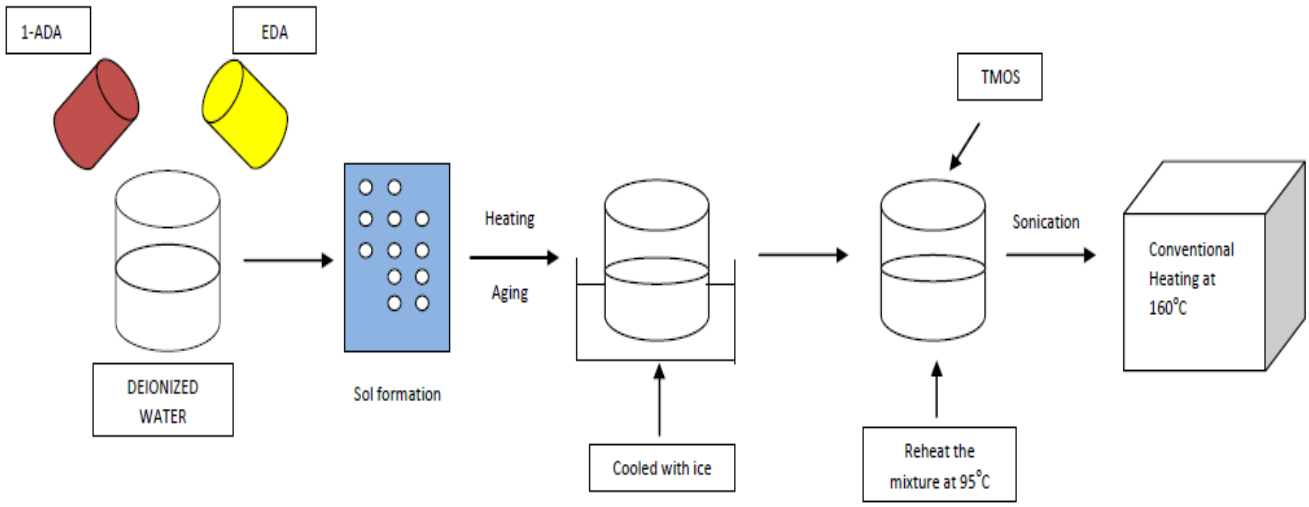

Figure 6: Graphic Illustration on Experimental Procedure

The chemical reagents used are tetramethoxysilane (Merck), structure directing agent (SDA) 1-adamantaneamine (Fisher Scientific > 96%), ethylenediamine (Merck) for maintaining pH and di-ionized water. Two reactant mixtures were prepared respectively by suspending 1.422g of 1-adamantaneamine (Fisher Scientific 96%) in 4.85g of ethylenediamine (Merck) in 40.464g of deionized water. A stirring bar was immersed into the solution and stirred with a magnetic stirred at 200rpm for 1 hour. After heating the mixture for 1 h at 95 ºC with continuous agitation, it was cooled down in ice for 20 min. Then, 3.044 g of tetramethoxysilane (Merck) was added drop by drop in ice cooled mixture. After that, the mixture was again heated for 3 h at 95 ºC with continuous agitation. The molar ratio of the final mixture solution was 1-adamantaneamine: Silica: Ethylenediamine: Water = 47:100:404:11240. The mixture is then sonicated by using an ultrasound equipment which produces acoustic waves at frequency of 137 kHz. The energy input of sonication was 550 W and kept for aging for require hours.

The mixture was then poured into Teflon-lined stainless steel autoclave. Hydrothermal crystallization was continued under autogenous pressure in an oven at 160ºC. After synthesis, the zeolite powders were recovered by centrifugation and washed thoroughly with deionized water until the pH of the washing liquid became neutral and then dried at 100ºC for further characterization.

In the present work, seven samples were synthesized using the same solution mixture, with different time of ultrasonic pre-treatment and hydrothermal growth. Samples 4-7 underwent ultrasonic pre-treatment for 1 h. Subsequently, these solution mixtures were heated in the pressure vessel for hydrothermal growth for 5 days, 2 days, 1 day and 0.5 day at 160 ºC respectively. For sample 3, the reaction mixture was sonicated for 2 h and then, heated in pressure vessel for hydrothermal growth for 5 days at 160 ºC. Sample 2 was sonicated for 3 h and it was heated in the pressure vessel for hydrothermal growth for 10 days at 160 ºC. The powder product was recovered by using centrifugation and repeated washed with deionized water followed by drying overnight at 100 ºC. For comparison, sample 1 was prepared by

using conventional heating method described by (Exter et al., 1997) without ultrasonic pre-treatment.

3.3 Characterization Study

The resulting crystals were characterized for its crystallinity and morphology using XRD and FESEM, respectively. XRD was carried out on Philips 1710 diffractometer using CuKα radiation (α = 1.541 Å) in the 2 theta range of 5–35° at ambient temperature. Morphology of DDR3 crystals was determined using scanning electron mircroscope (FESEM). The characteristics vibration bands for DDR3 crystals were examined by FTIR in KBr pellets.

3.4 CO_2 Physisorption Testing

The CO_2 adsorption capacity was measured at 298 K with a BELSORP Adsorption/Desorption Data Analysis Software (BEL Japan Inc.) for CO_2 Physisorption. Approximately 0.20 g of the adsorbent was used for each measurement, and the adsorption isotherm was measured at 101.3 kPa.

3.5 Project Activities

In FYP I, the project is mainly focus on the experiment of synthesizing the DDR zeolite particles by applying ultrasonic pretreatment method. Before experiment being conducted, proper procedures need to be done in term of the chemicals and equipment that will be used. Meanwhile, in FYP II is the continuation of synthesis the particles and the synthesized of particles are characterized to get for the morphology, crystallization, types of bonds as well as the adsorption capability.

3.5.1 Availability of chemicals

Table 4 shows the amount of chemicals needed for synthesizing DDR zeolite

Table 4: Amount of chemicals needed for synthesizing DDR zeolite

Chemical Name	Chemical Formula	molar ratio
1. 1-adamantanamine	$C_{10}H_{17}N$	47
2. ethylene diamine	$C_2H_8N_2$	404
3. water	H_2O	11240
4. silica (TMOS: Tetramethylsilicate)	SiO_2	100

3.5.2 Availability of apparatus/equipment

Table 5 shows the list of apparatus and equipment used for this experiment.

Table 5: List of apparatus and equipment

Apparatus
1. Beaker
2. Support tubes
3. Teflon-lined synthesis reactor
4. Ultrasonicator
5. Oven
6. Hot plate magnetic stirrer

3.5.3 Time Management

Time management is important in conducting an experiment as this is to make sure that the experimental can be preceded smoothly without overlapping with other's schedule. Time planning is done on all experimental runs with different hydrothermal growth synthesis time and ultrasonic durations. For example, experiment run for Sample 7 requires ultrasonic duration of 1 hour and hydrothermal growth of 12 hours (Refer to Table 6). Table 6 shows the estimation time to complete for Sample 7.

Table 6: Time Planning For Sample 7

Date	Task	Duration	Start	End
1st Day	Preparation for apparatus and chemicals	15 minutes	11.00 a.m	11.15 a.m
	Weighing chemicals	15 minutes	11.15 a.m	11.30 a.m
	Adding 1-ada and EDA into deionized water Stirring mixture	1 hr 30 minutes	11.30 a.m	1.00 p.m
	Heating mixture	1 hr	1.00 p.m	2.00 p.m
	Cooled down with ice	20 minutes	2.00 p.m	2.20 p.m
	Adding TMOS, heat again	3 hrs	2.20 p.m	5.20 p.m
	Ultrasound	1 hr	5.20 p.m	6.20 p.m
2nd Day	Oven for hydrothermal growth	12 hrs	6.20 p.m	7.00 a.m
	Cooled Down, Wash and Centrifuge	1 hr	7.00 a.m	8.00 a.m
	Drying in oven	24 hrs	8.00 a.m	8.00 a.m (3rd Day)

3.6 Key milestone

Table 7 shows the key milestone for FYP I and FYP II.

Table 7: Key milestone of FYP I and FYP II

	Task	Completion
May 2014	Selection of Project Topic	Week 2
	Preliminary research work	Week 5
	Submission of extended proposal	Week 5
	Proposal Defense	Week 9
	Submission of Interim Draft Report	Week 13
	Submission of Interim Draft Report	Week 14
September 2014	Synthesis of DDR particles	Week 1
	Submission of Progress Report	Week 8
	Project Work Continues	Week 9
	Pre-SEDEX	Week 11
	Submission of Draft Final Report	Week 12
	Submission of Dissertation	Week 13
	Submission of Technical Paper	Week 13
	Viva	Week 13
	Submission of Project Dissertation	Week 15

3.7 Gantt Chart

Table 8 and 9 show the Gantt chart for FYP I and FYP II, respectively.

Table 8: Gantt Chart for FYP I

Activities	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14
First meeting with coordinator and supervisor														
Problem Statement and analysis of project														
Preliminary research work and literature review														
Submission of extended proposal defense														
Oral proposal defense presentation														
Synthesis of DDR3 zeolite particles														
Preparation of Interim Report														
Submission of Interim Draft Report														
Submission of Interim Final Report														

Process

Suggested Key Milestone

Table 9: Gantt chart for FYP II

Activities	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15
Synthesis of DDR3 particles															
Submission of Progress Report															
Characterization study															
Pre-SEDEX															
Submission of Draft Final Report															
Submission of Dissertation															
Submission of Technical Paper															
Viva															
Submission of Project Dissertation															

Process

Suggested Key Milestone

CHAPTER 4: RESULTS AND DISCUSSION

4.1 X-Ray Diffraction (XRD)

Figure 7 shows the XRD patterns of samples S1-S7 synthesized in the present work. Referring to Figure 7, the presence of peaks in the XRD pattern of samples 1-6 confirmed the crystalline structure of DDR3. The significant peaks at 2theta values of 9 º, 17 º, 18 º, 19 º, 19.5 º and 20 º are consistent with those peaks reported in the literature for DDR3 structure (Tomita et al., 2004). However, referring to Figure 7, sample S7, shows the mixture of amorphous and crystalline structure due to the absence of major peaks at 2theta value of 9 º, 17 º, 18 º, 19 º, 19.5 º and 20 º. The structure of DDR3 crystals synthesized in the present work is summarized in Table 10.

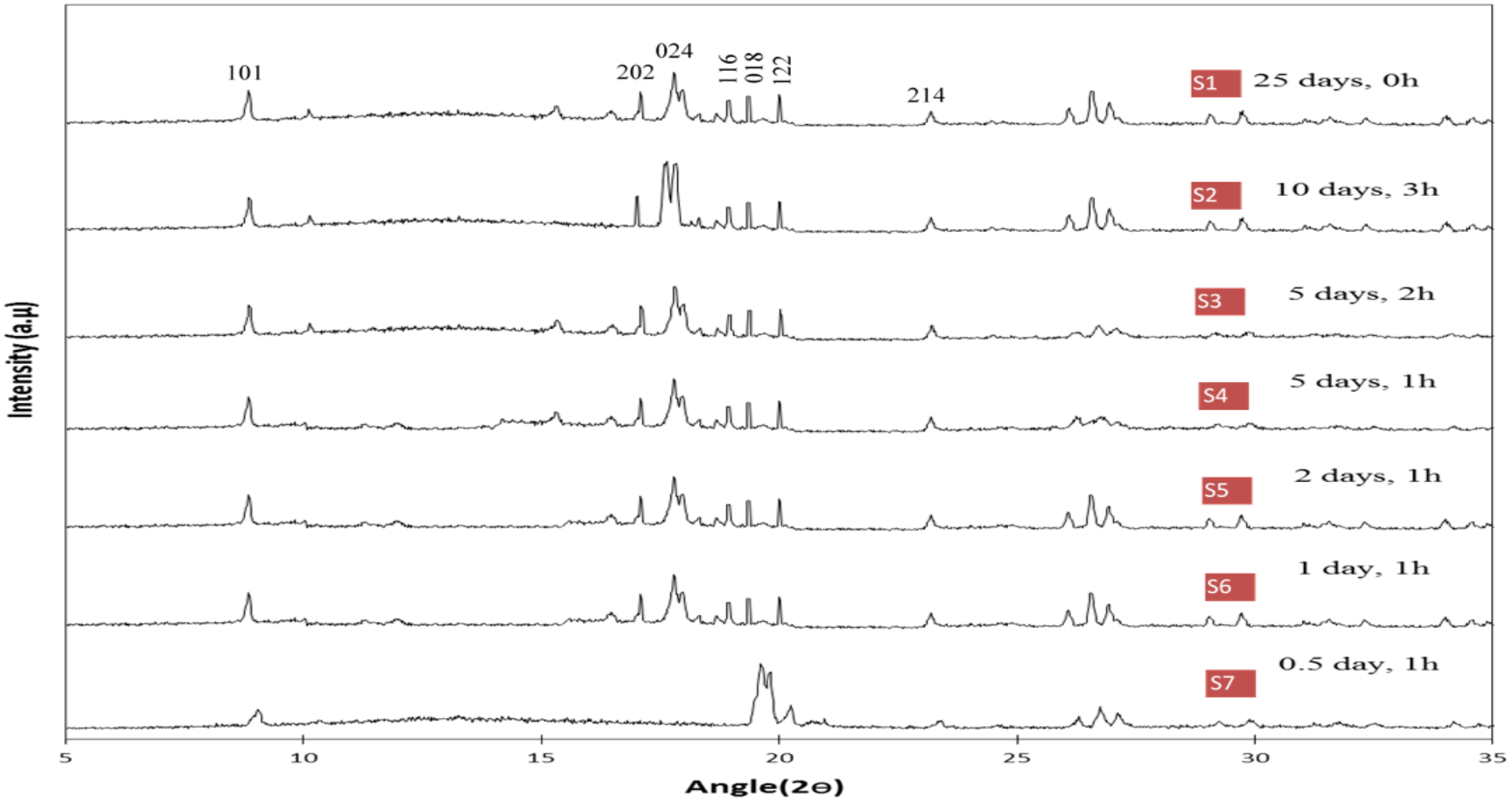

Figure 7: XRD pattern of all samples synthesized in the present work

Table 10: Structure of DDR3 crystals synthesized in the present work using ultrasonic pre-treatment coupled with conventional heating method

Samples	Sonication Time (h)	Heating Duration (days)	Structure
Sample 1	-	25	DDR3
Sample 2	3	10	DDR3
Sample 3	2	5	DDR3
Sample 4	1	5	DDR3
Sample 5	1	2	DDR3
Sample 6	1	1	DDR3
Sample 7	1	0.5	Amorphous +Sigma 2

Ultrasonic pre-treatment is not affecting the degree of crystallinity of samples S2 - S6 because XRD pattern of these samples showed similar peaks. Crystallinity of sample S2 is higher as compared to other DDR3 samples because XRD pattern shows higher peaks intensity at 2 theta value of 18º. These results show that ultrasonic pre-treatment is successfully reduced the synthesis duration of DDR3 zeolite crystals from 25 days to 1 day. This is because during ultrasonic pre-treatment of sol, the evolutions of energy collapses the solution bubbles and help in the formation of free radical, and thus, stimulate the reaction species which accelerates the nucleation and helps in crystal growth formation (Suslick, Doktycz, & Mason, 1990). In the sonication reaction, two Si $(OH)_4$ species come in contact to form Si–O–Si through a transition state. During formation of Si–O–Si, high activation energy formed under ultrasonic cavitation

followed by the removal of water molecules (Trinh, Rozanska, Delbecqa, & Sautet, 2012). The possible formation steps are shown in Figure 8.

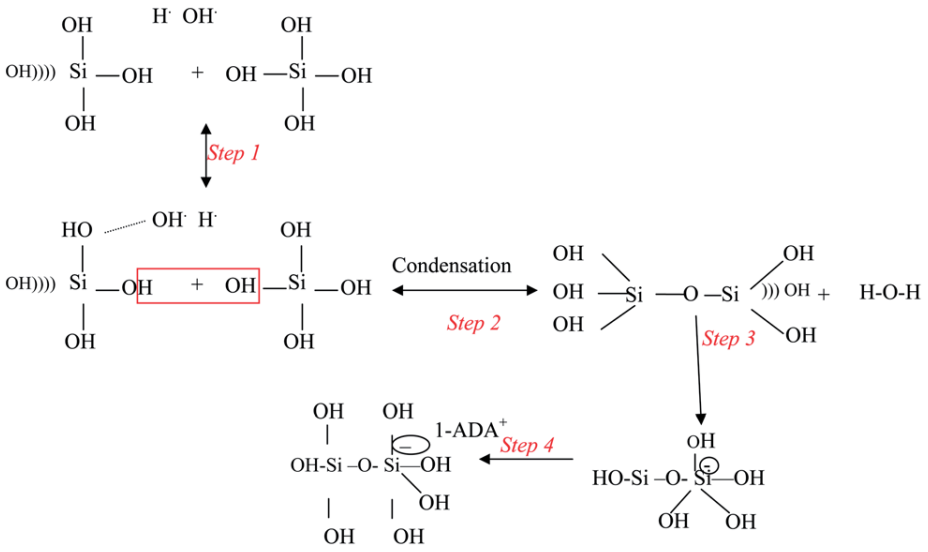

Figure 8: The possible formation steps of DDR3 structure during the ultrasonic pretreatment

As shown in Figure 8 the first step is the formation of Si–O–Si bond between two molecules and second step is the removal of H_2O molecule from the dimer species in the solution. In strong basic solution, the most stable species are $Si(OH)_4$. The two $Si(OH)_4$ combine to form Si–O–Si bond in transition state because the silicon acquires a proper negative charge the transition state, the anionic species OH should help in stabilizing the negative charges so that it can cross-linked and interact with cationic organic structure directing agent to form porous structure. In case of DDR3 synthesis, the reaction takes place under basic conditions, where the silica species are present as anions and cationic species is 1-adamantanamine which is used as structure directing agent. The schematic of the reaction is described by Figure 9 (Sen, Bose, Pal, Das, & Das, 2014).

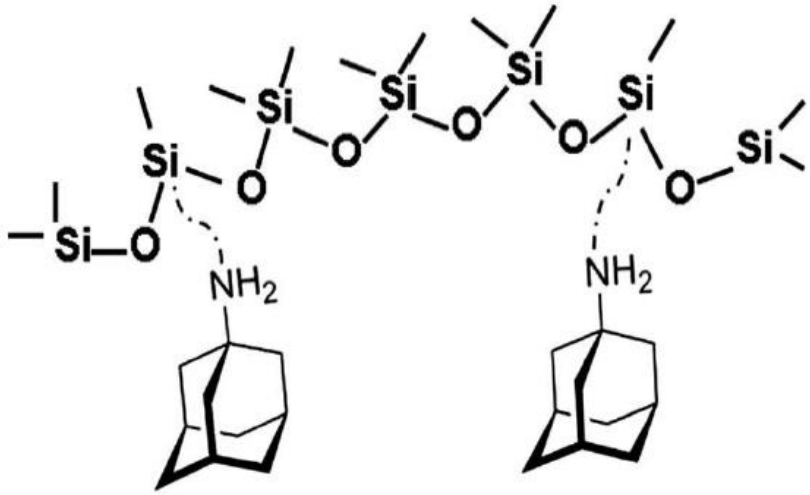

Figure 9: Schematic presentation of reaction between silica and 1-adamantanamine

From these results, it can be confirmed that crystals synthesized in 1 day at 160 ˚C with ultrasonic pre-treatment for 1 h demonstrated the structure of DDR3 topology. Synthesis of DDR3 crystals in 1 day is an appreciable short duration as compared to the values reported in literature. Therefore at least 1 day of the synthesis time is required to obtain fully crystalline DDR3 applying ultrasound wave in ultrasonic-assisted hydrothermal condition. Applying ultrasound not only induces nucleation, but also increases reproducibility. However, the precise mechanisms for ultrasound action on crystallization remain to be established. In fact, ultrasound can induce primary nucleation in nominally particle-free solutions and, noteworthy, at much lower supersaturation levels than would otherwise be the case. Another effect of ultrasound on nucleation is shortening the induction time between the establishment of supersaturation and the onset of nucleation and crystallization. In addition other postulates suggest that, subsequent rapid local cooling rates occurred after collapsing of bubbles, play a significant role in increasing supersaturation, in which case it should be possible to correlate the number of cavitation and nucleation events in a quantitative way (Mullin, 2001). It is shown ultrasound can enhance processes, chemical reactions, nucleation and

growth precipitates. It is extremely useful in crystallization processes since it can initiate seeding and control subsequent crystal growth in a saturated or supercooled medium (Amara, Ratsimba, Wilhelm, & Delmas, 2001; Thompson & Doraiswamy, 2000).

4.2 Field Emission Scanning Electron Microscope (FESEM)

All samples were characterized by using Field Emission Scanning Electron Microscope (FESEM) and Figure 10 compares the morphology of all samples. As shown in Figure 10, only sample S7 which synthesized using 12 h conventional heating showed morphology consisting the mixture of amorphous and crystalline structure. FESEM results of all samples are consistent with the XRD peaks shown in Figure 7.

Interestingly, applying ultrasound irradiation prior to synthesis is found to dramatically maintain the morphology of the resulting particles. In this case, uniform particles with size of about 2 μm are found except for sample S7. The obtained particles are homogenous and possess rough external surfaces with irregular shape. While FESEM image of sample S7 shows existence of a large amount of amorphous phase of undefined morphology. In this case, sigma 2 crystals were formed instead of DDR3. These morphology changes reveal that the type of driving force in the synthesis plays a crucial role in the shape and size control of DDR3 crystals. It shows that 12 hours is not sufficient to form fully crystalline DDR3 particles. At least 24 hours is needed to obtain a complete crystalline DDR3 and possess same morphology as compared to the sample S1.

Thus, it can be concluded that ultrasonic mediated hydrothermal technique can initiate seeding and control subsequent crystal growth. This is thought to be due to cavitation bubbles themselves acting as nuclei for crystal grows and to the disruption nuclei already present within the medium thus increasing the number of nuclei in the medium (Askari & Halladj, 2011).

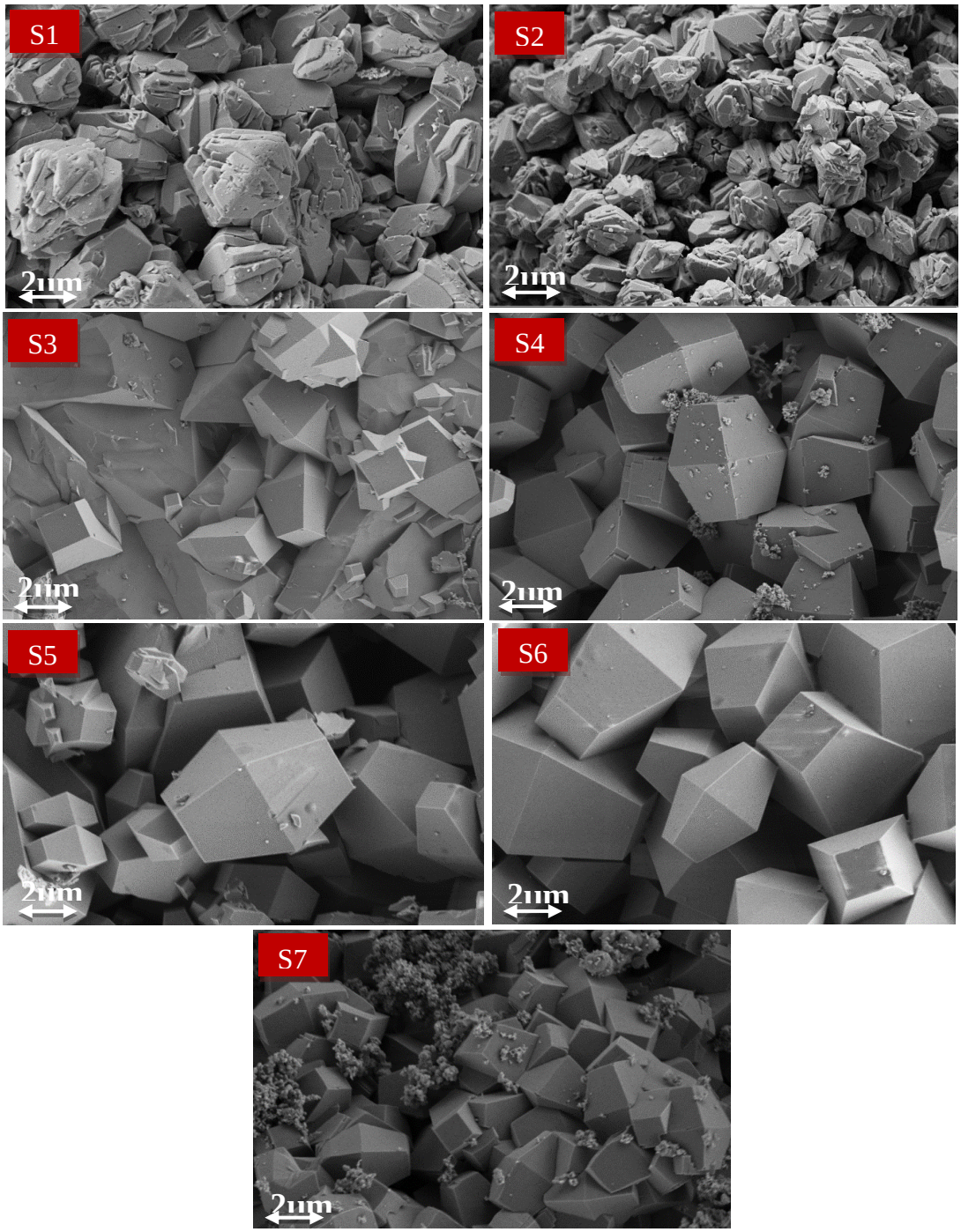

Figure 10: Scanning electron microscopy micrographs of all samples synthesized in the present work

4.3 Fourier Transformed Infared (FTIR)

Figure 11 shows the IR spectra of all samples synthesized in the present work. Spectra of sample S1 showed strong vibration at 3372 cm^{-1}, 1579 cm^{-1}, 1484 cm^{-1}, 1326cm^{-1}, 1100cm^{-1}, 788 cm^{-1}, 725cm^{-1}, 548cm^{-1} and 467cm^{-1}. The characteristic peaks at 788 cm^{-1} and 467 cm^{-1} were attributed to O–Si–O and Si–O tetrahedral bonding, respectively (Man & Santen, 1992). In addition, the appearance of the peaks at 725 cm^{-1} and 1579 cm^{-1} were assigned to the external linkage and vibration of water molecule, respectively (Man & Santen, 1992). The peaks identified at 3372 cm^{-1}, 1484 cm^{-1}, 1326 cm^{-1} and 1100 cm^{-1} are correspond to the symmetric stretching vibration of 1-adamantanamine (Man & Santen, 1992). Furthermore, the vibration of internal tetrahedron was shown at 548 cm^{-1}. IR analysis of sample 1 shows similar vibration as described for DDR3 crystals in literature (Sen et al., 2014). It can be observed that the IR peaks of samples S2 - S6 showed similar vibration as described in sample S1 and confirmed DDR3 topology. However, IR spectra of the sample S7 synthesized in 0.5 days with 1 h sonication did not show the bending as described for DDR3 topology. This is because the IR spectra of sample S7 did not show the characteristic peaks at 3720 cm^{-1}, 1579 cm^{-1}, 1484 cm^{-1} and 1326cm^{-1}. IR analyses are consistent with the observation as described in XRD and Field Emission Scanning Electron Microscope.

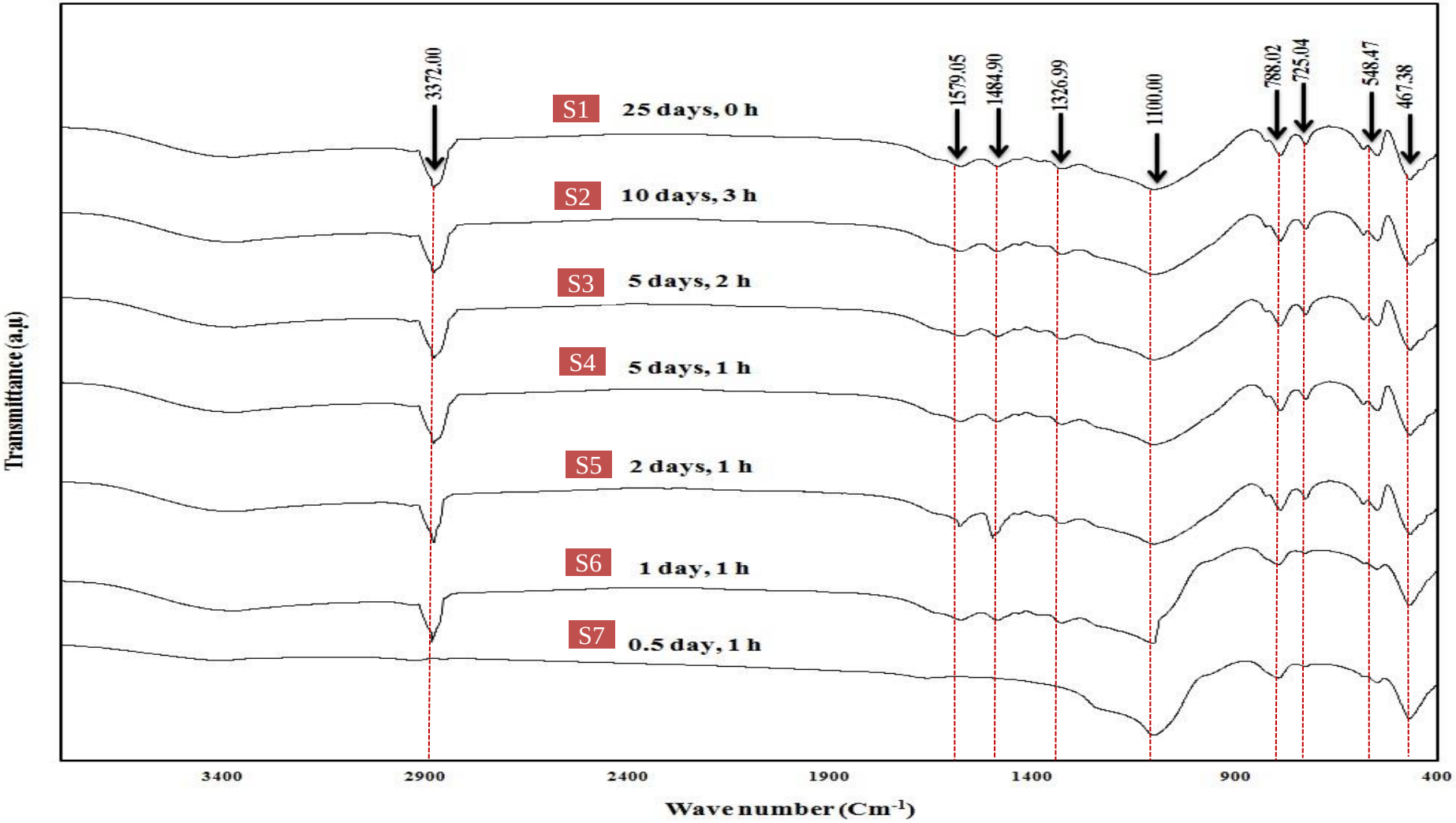

Figure 11: IR spectra of all samples synthesized in the present work

4.4 CO_2 Adsorption Capability (BELSORP)

Table 11 shows the CO_2 adsorption capacity of resulting particles for all samples measured at 298 K and 101.3 kPa. The adsorption isotherms of all the resulting particles are shown in Figure 12. Referring to Figure 12, the isotherm of carbon dioxide for all-silica DDR3 demonstrated Type I according to Brunauer classification, which is expected for adsorption of small adsorbates on a microporous adsorbent (Brunauer, Deming, Deming, & Teller, 1940).

Den Exter et al. (1996) measured the adsorption isotherm of CO_2 on DDR3 at 296 K and 101 kPa. The results showed that the respective adsorbed amounts of CO_2 was 1.764 mol/kg. Meanwhile, Himeno et al. reported the respective amounts of adsorbed CO_2 on the DDR crystal was 1.2 mol/kg (Himeno, Tomita, Nakayama, Yajima, & Yoshida, 2007). As referring to Figure 13, the CO_2 adsorption amounts for sample S2, S3, S4, S5, S6, S7 are 0.052771, 0.009273, 0.021204, 0.007369, 0.006901, and 0.017676 mol/kg, respectively. Therefore, it can be seen that the result showed low relatively adsorption due to different method of capacity measurement. However, sample S2 shows the highest adsorption capacity mainly because of its longest synthesis duration of 10 days.

Table 11: CO_2 adsorption capacity of resulting particles

Sample	CO_2 adsorption capacity (mol/kg)
1	1.2
2	0.052271
3	0.009273
4	0.021204
5	0.007369
6	0.006901
7	0.017676

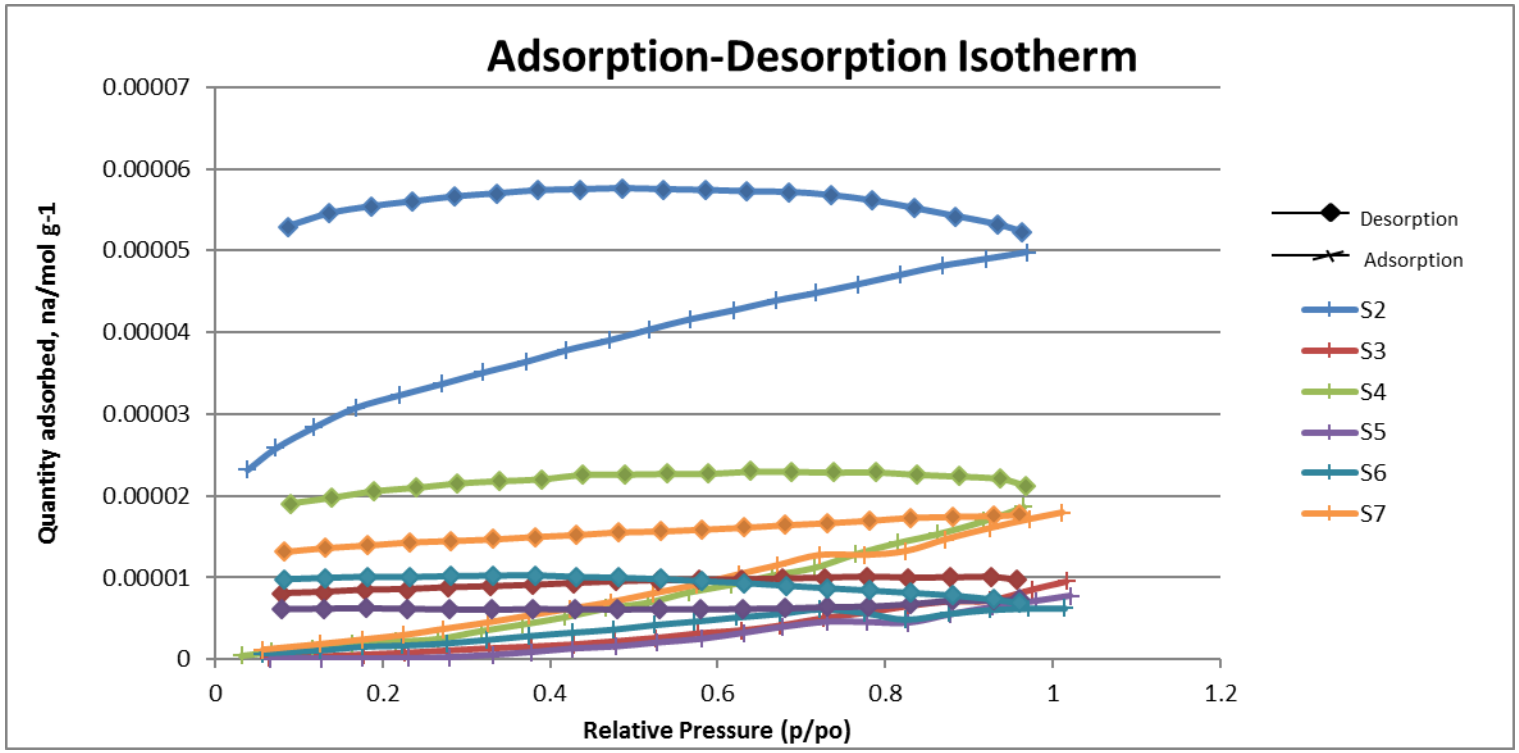

Figure 12: Adsorption-Desorption Isotherm

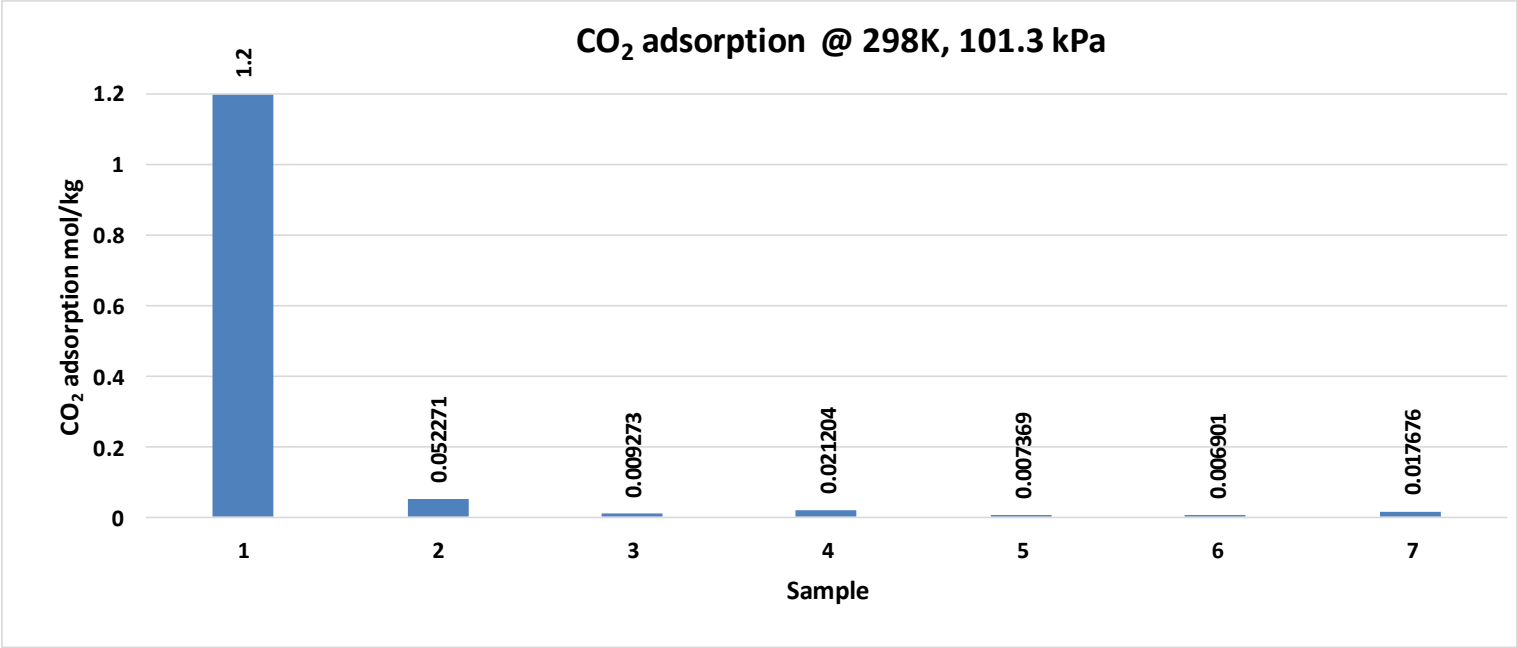

Figure 13: CO_2 adsorption of resulting particles at 298K, 101.33 kPa (the adsorbed amount for sample 1 is obtained from Himeno et al. [42])

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

CO_2 emission gives a major impact on global climate change. Many technologies that been developed by researchers to reduce this emission. Membrane separation, absorption and adsorption can be used as CO_2 captures. The ideal way to capture this CO_2 is by implementing adsorption process. In this project, DDR3 zeolite is chosen as adsorbent. Main reason from this is that the pores of the zeolite are in the same order as the size of the CO_2 molecule. In this way, good sieving properties are expected towards large molecule impurities.

In the present research, DDR3 zeolite was synthesized using ultrasonic pretreatment as this method is most feasible in term of reducing the crystallization time. Then, the resultant DDR3 zeolite particles were characterized by using XDR, FESEM and FTIR. Meanwhile, in order to determine the CO_2, adsorption characteristic of DDR3 zeolite CO_2 physisorption testing (BELSORP) were conducted.

In summary, we have successfully synthesized DDR3 zeolite by ultrasonic pretreatment coupled with a hydrothermal heating method. Ultrasonic pre-treatment of mixture solution prior to hydrothermal synthesis facilitates the formation of active radicals which are responsible for rapid crystallization of zeolite phase. The XRD, FESEM and FTIR confirmed the formation of DDR3 zeolite.

The XRD patterns of all the synthesized samples except sample S7 matches well with those of DDR3 structures reported in literature. The significant peaks at 2theta values of 9^{o}, 17^{o}, 18^{o}, 19^{o}, 19.5^{o} and 20^{o} values are consistent with those peaks reported in the literature for DDR3 structure. FESEM results of all samples are consistent with the XRD peaks. Also, FTIR spectra of all samples showed strong vibration at 3372 cm^{-1}, 1579 cm^{-}

[1], 1484 cm^{-1}, 1326cm^{-1}, 1100cm^{-1}, 788 cm^{-1}, 725cm^{-1}, 548cm^{-1} and 467cm^{-1}. This shows significant effect on crystallization time and phase formation of DDR3 zeolite. This method also enhances the rate of crystallization and as a result, synthesis time of DDR3 zeolite has been reduced 1 day instead of 25 days. However, the adsorption capability showed low relatively adsorption due to different method of capacity measurement used.

Nevertheless, the synthesis period is very short; therefore this process of sonication is beneficial for synthesis of DDR3 zeolite.

5.2 RECOMMENDATION AND FUTURE WORK

For further expansion of project, some of recommendations can be proposed are:

1. The DDR3 crystals can be used for preparation of DDR3 membranes

   A substantial reduction of the synthesis time combined with full conversion of the sol into zeolite material at short crystallization time would make the synthesis very useful for DDR3 zeolite membrane. This is because the preparation of DDR3 zeolite membranes are time consuming besides the process required for synthesis the support (crystal) typically from 25 days to 42 days. Therefore, the importance of sonication method to reduce the synthesis duration of DDR3 crystal prior to membrane formation is very crucial in order to reduce the overall synthesis duration of DDR3 membrane.

2. Using microwave heating instead of hydrothermal growth heating

   It has been reporting that a microwave-hydrothermal heating technique was superior compared to conventional hydrothermal heating in reducing the time period for crystallization. Due to the shorter residence times, higher purity products can be achieved. Therefore for future work, the study of effects crystallization time in synthesizing DDR3 by using microwave heating is highly recommended.

3. Proper CO_2 adsorption equipment need to be used

   The inconsistency of adsorption capacities result is due to the different measurement used. Therefore, it is recommended to test on the same method used from literature so that the result can be achieved as compared to reported value.

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